

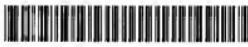


(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 965 657 A1

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:  
22.12.1999 Bulletin 1999/51

(51) Int Cl. C23F 11/14, C23F 11/04,  
C23F 11/12

(21) Application number: 99304781.0

(22) Date of filing: 18.06.1999

(84) Designated Contracting States:  
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE  
Designated Extension States:  
AL LT LV MK RO SI

(30) Priority: 19.06.1998 US 99704

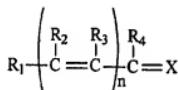
(71) Applicants:  
• Halliburton Energy Services, Inc.  
Duncan, Oklahoma 73536 (US)  
• Nalco/Exxon Energy Chemicals, L.P.  
Sugar Land, Texas 77478-2121 (US)

(72) Inventors:  
• Houston, Grahame N.  
Houston, Texas 77040 (US)  
• Williams, Dennis A.  
Houston, Texas 77062 (US)  
• Cassidy, Juanita M.  
Duncan, Oklahoma 73533 (US)  
• Funkhouser, Gary P.  
Duncan, Oklahoma 73533 (US)

(74) Representative: Wain, Christopher Paul et al  
A.A. Thornton & Co.  
235 High Holborn  
London WC1V 7LE (GB)

## (54) Corrosion inhibiting compositions

(57) A corrosion inhibiting aqueous composition comprises one or more aldehyde oligomers having the general formula



wherein  $\text{R}_1$  is phenyl or substituted phenyl,  $\text{R}_2$  and  $\text{R}_3$  are each hydrogen, a saturated or unsaturated aliphatic group or an aryl group,  $\text{R}_4$  is hydrogen,  $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$  where  $m$  is from 0 to 5, or a tris(2-aminocethyl)amine group,  $\text{X}$  is oxygen or  $=\text{NH}$ , and each of the above may also be any other value which does not adversely affect the composition. The compositions are for addition to corrosive aqueous acid solutions to reduce or inhibit the corrosive effects thereof on metal surfaces.

EP 0 965 657 A1

## Description

[0001] The present invention relates to a composition for addition to a corrosive aqueous acid to reduce or inhibit its corrosive effect on metal surfaces.

5 [0002] Subterranean hydrocarbon-containing formations penetrated by well bores are often treated with aqueous acids to stimulate the production of hydrocarbons therefrom. One such treatment, generally referred to as "acidizing", involves the introduction of an aqueous acid solution into a subterranean formation under pressure so that the acid solution flows through the pore spaces of the formation. The acid reacts with acid-soluble materials contained in the formation thereby increasing the size of the pore spaces and increasing the permeability of the formation. Another 10 production stimulation treatment known as "fracture-acidizing" involves the formation of one or more fractures in the formation and the introduction of an aqueous acid solution into the fractures to etch the fracture faces, whereby channels are formed therein when the fractures close. The acid also enlarges the pore spaces in the fracture faces and in the formation.

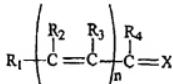
[0003] While acidizing and fracture-acidizing well stimulation treatments have been performed successfully for many 15 years, a continuous problem which accompanies the treatments is the corrosion of metal surfaces in pumps, tubular goods and equipment used to introduce aqueous acid solutions into the subterranean formations to be treated. The expense associated with repairing or replacing corrosion damaged tubular goods and equipment can be very high. The corrosion of tubular goods and down-hole equipment is increased by the elevated temperatures encountered in deep formations, and the corrosion results in at least the partial neutralization of the acid before it reacts with acid-soluble materials in the formations.

20 [0004] Aqueous acid solutions are also utilized in a variety of other industrial applications to contact and react with acid soluble materials. In such applications, metal surfaces are necessarily also contacted with the acid and any corrosion of the metal surfaces is highly undesirable. In addition, other corrosive fluids such as aqueous alkaline solutions, heavy brines, petroleum streams containing acidic materials and the like are commonly transported through and corrode metal surfaces in tubular goods, pipelines and pumping equipment.

25 [0005] A variety of metal corrosion inhibiting compositions and formulations which can be added to aqueous corrosive fluids have been developed and used heretofore. While such compositions and formulations have achieved varying degrees of success in preventing corrosion of metal surfaces, there is a continuing need for improved metal corrosion inhibiting compositions which are effective when combined with aqueous corrosive fluids of the types described above and which provide greater and more reliable corrosion inhibition than has heretofore been possible.

30 [0006] We have now devised some compositions which, when added to aqueous corrosive fluids such as inorganic or organic acids, reduce or inhibit the corrosive effect thereof on metal surfaces.

[0007] In one aspect, the invention provides a composition for addition to a corrosive aqueous fluid to reduce or 35 inhibit its corrosive effect on metal surfaces, which composition comprises one or more aldehyde oligomers having the general formula:



45 wherein  $\text{R}_1$  is a substituted or unsubstituted phenyl group, preferred substituents (when present) being methyl, hydroxyl or methoxy groups or other substituents which do not have an adverse effect;  $\text{R}_2$  and  $\text{R}_3$  are individually hydrogen, a saturated or unsaturated aliphatic group having from 1 to about 12 carbon atoms, an aryl group or a halide, hydroxyl or alkoxy group;  $\text{R}_4$  is hydrogen,  $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-$  or  $-\text{CH}_2-\text{CH}_2-\text{NH}_2$  where  $\text{m}$  is 0 or an integer in the range of from 1 to 5, a tri(2-aminocetyl)amine group, or together with the  $-\text{C}=\text{X}$  forms an imidazoline ring;  $\text{n}$  is an integer of from 2 to 7; and  $\text{X}$  is oxygen,  $\text{NH}$  or with  $\text{C}$  and  $\text{R}_4$  is part of an imidazoline ring.

50 [0008] The invention also includes an aqueous acid solution containing a composition of the invention.

[0009] The compositions of the present invention are based on the discovery that certain aldehyde oligomers formed, for example, by the condensation reaction of benzaldehyde and acetaldehyde, provide unexpected increased corrosion inhibition when added to corrosive aqueous fluids as compared to prior art corrosion inhibiting compositions including aldehydes. Surprisingly, the aldehyde oligomers of this invention can be utilized directly in corrosive aqueous fluids without the use of a dispersing surfactant or mutual solvent. However, in preferred corrosion inhibiting compositions of this invention, a dispersing surfactant or a mutual solvent or both are included in the compositions.

[0010] As mentioned, the above described corrosion inhibiting composition can include a dispersing surfactant or a mutual solvent, or both, and in addition, one or more quaternary ammonium compounds, one or more corrosion inhibitor activators and other components commonly utilized in corrosion inhibiting formulations.

[0011] The compositions of the present invention are basically comprised of one or more aldehyde oligomers preferably formed by the condensation reaction between a benzaldehyde and acetaldehyde or a derivative. It has been discovered that such oligomers provide surprisingly improved protection to metal surfaces from corrosion by corrosive aqueous fluids when one or more of the oligomers are combined with the corrosive aqueous fluids.

[0012] The aldehyde oligomers formed by the above described reaction which provide improved corrosion protection to metal surfaces have the formula given above. The benzaldehyde and/or acetaldehyde can contain substituents which do not have an adverse effect, i.e. which do not adversely interfere with the corrosion protection provided by the aldehyde oligomers and/or add to the corrosion protection provided. Examples of such substituents are halides, hydroxyl groups, alkoxy groups, hydrogen, aminalkylamine groups, imidazoline groups and the like. The most preferred aldehyde oligomers as described above are those wherein R<sub>1</sub> is phenyl, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are hydrogen, X is oxygen and n is 2 or 3.

[0013] The compositions of this invention can include a surfactant for dispersing the aldehyde in a corrosive aqueous fluid. Examples of suitable such dispersing surfactants are alkoxylated fatty acids, alkylphenol alkoxylates and ethoxylated alkyl amines. When a dispersing surfactant of the type described above is utilized in a corrosion inhibiting composition of this invention, it is generally present in the composition in an amount of from 1% to 45% by weight of the composition.

[0014] Another component which can be included in the corrosion inhibiting compositions is a solvent for the aldehyde oligomers which also dissolves in water, referred to herein as a "mutual solvent". Examples of such solvents are methyl alcohol, ethyl alcohol, isopropyl alcohol, ethylene glycol, propylene glycol, dimethyl formamide, N-methyl pyrrolidone, propylene glycol methyl ether and butyl cellosolve. When a mutual solvent of the type described above is included in a corrosion inhibiting composition of this invention, it is generally present in an amount of from about 1% to about 40% by weight of the composition.

[0015] In addition, the corrosion inhibiting compositions can include one or more quaternary ammonium compounds, one or more corrosion inhibitor activators and other components commonly utilized in corrosion inhibiting formulations such as acetylenic alcohols, Mannich condensation products formed by reacting an aldehyde, a carbonyl containing compound and a nitrogen containing compound, unsaturated carbonyl compounds, unsaturated ether compounds, formamide, formic acid, other sources of carbonyl, iodoles, terpenes, and aromatic hydrocarbons.

[0016] The quaternary ammonium compounds which function as corrosion inhibitors and can be utilized in accordance with the present invention have the general formula:



wherein each R is the same or a different group selected from long chain alkyl groups, cycloalkyl groups, aryl groups or heterocyclic groups, and X is an anion such as a halide. The term "long chain" is used herein to mean hydrocarbon groups having in the range of from about 12 to about 20 carbon atoms.

[0017] Examples of quaternary ammonium compounds which can be included in the corrosion inhibiting composition of this invention are N-alkyl, N-cycloalkyl and N-alkylarylpypnidium halides such as N-cylohexylpyridinium bromide or chloride, N-alkyl, N-cycloalkyl and N-alkylarylquinolinium halides such as N-dodecylquinolinium bromide or chloride, and the like. When a quaternary ammonium compound is included in a composition of this invention, it is generally present in an amount in the range of from about 1% to about 45% by weight of the composition.

[0018] Corrosion inhibitor activators function to activate corrosion inhibitor components such as quaternary ammonium compounds so that they function as corrosion inhibitors. Examples of such corrosion inhibitor activators which can be utilized in accordance with the present invention are cuprous iodide; cuprous chloride; antimony compounds such as antimony oxides, antimony halides, antimony tartrate, antimony citrate, alkali metal salts of antimony tartrate and antimony citrate, alkali metal salts of pyranoantimonate and antimony adducts of ethylene glycol; bismuth compounds such as bismuth oxides, bismuth halides, bismuth tartrate, bismuth citrate, alkali metal salts of bismuth tartrate and bismuth citrate; iodine; iodide compounds; formic acid; and mixtures of the foregoing activators such as a mixture of formic acid and potassium iodide. When a corrosion inhibitor activator is included in a composition of this invention, it is generally present in an amount in the range of from about 0.1% to about 5.0% by weight of the composition.

[0019] As mentioned above, the corrosive aqueous fluids in which the corrosion inhibiting compositions of this invention are effective include aqueous solutions of inorganic acids, organic acids and mixtures thereof as well as aqueous alkaline solutions, heavy brine and hydrocarbons containing corrosive materials. The metals which can be protected from corrosion by the corrosion inhibiting compositions include, but are not limited to, ferrous metals such as iron and steel and nonferrous metals such as aluminum, zinc and copper.

[0020] In order to inhibit the corrosion of metal surfaces of the types described above by a corrosive aqueous fluid, a corrosion inhibiting composition of this invention is combined with the corrosive aqueous fluid in an amount in the range of from about 0.05% to about 5% by weight of the corrosive aqueous fluid.

5 [0021] A metal corrosion inhibited aqueous acid composition of this invention for use in applications such as acidizing and fracture-acidizing is comprised of water, an acid selected from the group consisting of inorganic acids, organic acids and mixtures thereof, and at least one aldehyde oligomer as defined above.

[0022] The acid utilized in the aqueous acid compositions of this invention is generally present in the composition in an amount in the range of from about 1% to about 30% by weight of water therein with the aldehyde oligomer or oligomers being present in an amount in the range of from about 0.01% to about 2% by weight of the water.

10 [0023] The aqueous acid compositions can also include a dispersing surfactant of the type described above in an amount in the range of from about 0.001% to about 10% by weight of the water in the compositions, and/or a mutual solvent of the type described above present in the compositions in an amount in the range of from about 0.001% to about 30% by weight of water.

15 [0024] The compositions can also include one or more quaternary ammonium compounds of the type described above present in an amount in the range of from about 0.001% to about 10% by weight of water in the compositions, and one or more corrosion inhibitor activators of the type described above present in an amount in the range of from about 0.001% to about 5% by weight of water in the composition. Other corrosion inhibiting components known to those skilled in the art can also be included in the aqueous acid compositions. As mentioned above, the most preferred aldehyde oligomers for use in the aqueous acid compositions of this invention are those wherein R<sub>1</sub> is phenyl, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are hydrogen, X is oxygen and n is 2 or 3.

[0025] The methods of this invention for inhibiting the corrosion of metal surfaces by a corrosive aqueous fluid basically comprise combining a corrosion inhibiting composition of this invention as described above with the corrosive aqueous fluid in the general amount of from about 0.05% to about 5% by weight of the corrosive aqueous fluid.

[0026] The aldehyde oligomers described above which are useful in accordance with this invention can be synthesized in accordance with the following procedure. 16 parts by weight benzaldehyde are suspended in 100 parts by weight of a 1 to 10 mass percent aqueous catalyst A and 100 parts by weight of a 1 to 10 mass percent catalyst B. Catalyst A and B are of the general formulae M(OH)<sub>x</sub> and/or M(OR<sub>1</sub>)<sub>x</sub> wherein M is any group I or II metal and R<sub>1</sub> is an acyl group having 1 to 8 carbon atoms. The suspension is rapidly stirred and heated to a temperature ranging from about 25°C to about 70°C. From about 13.2 parts by weight to about 52.8 parts by weight acetaldehyde is predissolved

30 in from about 20 to about 50 parts by weight water. The resulting aqueous solution is slowly added to the benzaldehyde suspension at a rate between about 0.005 and 2 milliliters per minute. After the addition has been completed, the suspension is stirred for a period up to about ten hours. The reaction product in the form of a lower oily layer is partitioned between an aqueous basic layer and an organic layer. The organic phase is dried and the thick dark orange viscous oil product is recovered.

35 [0027] In order to further illustrate the corrosion inhibiting compositions and methods of the present invention the following examples are given.

#### EXAMPLE 1

40 [0028] Synthesis reactions were carried out to produce aldehyde oligomers of the formula set forth above wherein n was 2 or more. Certain of the resulting aldehyde oligomers produced were added in amounts of 0.5 grams to 5 milliliter amounts of methyl alcohol combined with a polysorbate dispersing surfactant in a volume ratio of 4:1. Hydrochloric acid and water were then added to the oligomer solutions to produce aqueous 15% by weight hydrochloric acid solutions containing the oligomers. To test the corrosion inhibiting effectiveness of the oligomers, the test hydrochloric acid solutions were heated to 150°F, and N-80 carbon steel corrosion coupons were immersed in the solutions for time periods of approximately two and one-half hours while maintaining the temperatures of the solutions at 150°F. Corrosion rates were measured electrochemically by a combination of linear polarization resistance and Tafel measurements and are expressed in milli-inches per year (MPY) units.

45 [0029] For comparative purposes, an  $\alpha, \beta$  - unsaturated aldehyde utilized heretofore as a component in a corrosion inhibiting composition and described in U.S. Patent No. 4,734,259 issued to Frenier, et al. on March 29, 1988, i.e., cinnamaldehyde, was also tested following the identical procedure described above.

50 [0030] The result of these tests are set forth in Table I below.

TABLE I

CORROSION TESTS			
	Aldehyde or Aldehyde Oligomer Tested	Solubility Observation	Corrosion Rate, MPY
5	C <sub>6</sub> H <sub>5</sub> - ICH=CH <sub>2</sub> - CH = O	Clear	3.8 (5.6) <sup>1</sup>
	C <sub>6</sub> H <sub>5</sub> - [CH=CH] <sub>2</sub> - CH = O	Cloudy	4.4 (3.4) <sup>1</sup>
10	C <sub>6</sub> H <sub>5</sub> - [CH=CH] <sub>3</sub> - CH = O	Cloudy	11 (12) <sup>1</sup>
	C <sub>6</sub> H <sub>5</sub> - [CH=CH] <sub>4</sub> - CH = O	Cloudy	8.9 (10) <sup>1</sup>
	C <sub>6</sub> H <sub>5</sub> - [CH=CH] <sub>5</sub> - CH = O	Cloudy	9.0 (13) <sup>1</sup>
	C <sub>6</sub> H <sub>5</sub> - [CH=CH] <sub>6</sub> - CH = O	Cloudy	34 (35) <sup>1</sup>
	Cinnamaldehyde	Cloudy	21

<sup>1</sup> A second test result is shown in parentheses

15

[0031] From the test results shown in Table I, it can be seen that the aldehyde oligomers utilized in accordance with the present invention provide improved corrosion protection as compared to the  $\alpha,\beta$  - unsaturated aldehyde, i.e., cinnamaldehyde.

20

#### EXAMPLE 2

25

[0032] A corrosion test was performed using an aldehyde oligomer of this invention synthesized with a 1:4 ratio of bezaldehyde to acetaldehyde. The test procedure utilized was the same as described in Example 1 above except that the methyl alcohol mutual solvent and the dispersing surfactant were omitted. That is, 0.5 grams of the oligomer were mixed with water and hydrochloric acid to make a 15% by weight acid solution which was tested as described in Example 1. The results of this test is set forth in Table II below.

TABLE II

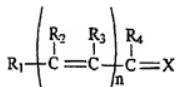
	Aldehyde Oligomer Tested	Solubility Observation	Corrosion Rate, MPY
30	C <sub>6</sub> H <sub>5</sub> - [CH=CH] <sub>4</sub> - CH = O	non-dispersed	3.8

#### Claims

35

1. A composition for addition to a corrosive aqueous fluid to reduce or inhibit its corrosive effect on metal surfaces, which composition comprises one or more aldehyde oligomers having the general formula:

40



45

wherein, R<sub>1</sub> is a substituted or unsubstituted phenyl group; R<sub>2</sub> and R<sub>3</sub> are individually hydrogen, a saturated or unsaturated aliphatic group having from 1 to about 12 carbon atoms, an aryl group or a halide, hydroxyl or alkoxy group; R<sub>4</sub> is hydrogen, -(NH-CH<sub>2</sub>-CH<sub>2</sub>)<sub>m</sub>-NH-CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> where m is 0 or an integer in the range of from 1 to 5, a tris(2-aminoethyl)amine group, or together with the C=X forms an imidazoline ring; n is an integer of from 2 to 7; and X is oxygen, NH or with C and R<sub>4</sub> forms an imidazoline ring.

50

2. A composition according to claim 1, which further comprises a surfactant.
3. A composition according to claim 2, wherein the surfactant is an alkoxylated fatty acid, alkylphenol alkoxylate or ethoxylated alkyl amine.
4. A composition according to claim 1, 2 or 3, which further comprises a solvent for said aldehyde oligomers, which

solvent also dissolves in water.

5. A composition according to claim 4, wherein said solvent is methyl alcohol, ethyl alcohol, isopropyl alcohol, ethylene glycol, propylene glycol methyl ether or butyl cellosolve.
6. A composition according to any of claims 1 to 5, which further comprises one or more quaternary ammonium compounds and/or a corrosion inhibitor activator.
10. 7. A composition according to claim 6, wherein the corrosion inhibitor activator is cuprous iodide, cuprous chloride, antimony compounds, bismuth compounds, iodine, iodide compounds, formic acid or any mixture of two or more thereof.
8. A composition according to any of claims 1 to 7, wherein R<sub>1</sub> is phenyl, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are hydrogen, X is oxygen and n is 2 or 3.
15. 9. A composition according to claim 1, wherein at least one of the aldehyde oligomers is the product of condensation between a substituted or unsubstituted benzaldehyde and acetaldehyde or a substituted acetaldehyde.
20. 10. An aqueous fluid which comprises at least one inorganic or organic acid or any mixture of two or more thereof, and from 1 to 30% by weight of the water, of a composition as claimed in any of claims 1 to 9.

25

30

35

40

45

50

55



DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	GROWCOCK F B ET AL: "INHIBITION OF STEEL CORROSION IN HCl BY DERIVATIVES OF CINNAMALDEHYDE. PART II. STRUCTURE-ACTIVITY CORRELATIONS" CORROSION, vol. 45, no. 12, 1 December 1989 (1989-12-01), pages 1007-1015, XP000115785 ISSN: 0010-9312 * page 1008; table 7 * * table 7 *	1,2,6, 8-10
Y	US 4 734 259 A (FRENIER WAYNE W ET AL) 29 March 1988 (1988-03-29) * page 4, line 33 - page 5, line 60; claim 1 *	3-5,7
D,Y	EP 0 593 230 A (HALLIBURTON CO) 20 April 1994 (1994-04-20) * page 4, line 1-5; claim 1 *	3
Y	US 3 589 860 A (FOROUIS ZISIS ANDREW) 29 June 1971 (1971-06-29) * column 4, line 58-69 *	4,5,7
X	US 4 980 074 A (HENSON EDWIN R ET AL) 25 December 1990 (1990-12-25) * claim 1 *	1,10
X	US 2 571 739 A (MARSH G. A.) 16 October 1951 (1951-10-16) ***	1
A		
The present search report has been drawn up for all claims		
Place of search	Date of completion of the search	Examiner
THE HAGUE	20 September 1999	Torfs, F
CATEGORY OF CITED DOCUMENTS		
X : primary document taken alone	T : theory or principle underlying the invention	
Y : particularly relevant document combined with another document of the same category	E : earlier patent document, but published on, or after the filing date	
A : technological background	D : document forming the application	
O : non-written disclosure	L : document cited for other reasons	
P : intermediate document	& : member of the same patent family, corresponding document	

ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 99 30 4781

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EPO file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

20-09-1999

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 4734259 A	29-03-1988	CA	1259481 A	19-09-1989
		EP	0289665 A	09-11-1988
EP 0593230 A	20-04-1994	NONE		
US 3589860 A	29-06-1971	NONE		
US 4980074 A	25-12-1990	NONE		
US 2571739 A	16-10-1951	NONE		

EPO FORM P005  
For more details about this annex : see Official Journal of the European Patent Office, No. 12/82